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Binder Free Graphene Hybridized Fe_3O_4 Nanoparticles for Supercapacitor Applications

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Introduction

In a world with increasing energy demands, the need for safe and mobile energy storage grows. There are a number of renewable energy sources that can be harvested, however peak demand and peak production times tend to not overlap. As the capabilities of collecting the energy grows so does the need to store the energy for later consumption. The two promising methods of storing energy are batteries or supercapacitors. Both technologies employ an electrode consisting of an active material bound to a current collector. This material participates in a redox reaction, storing charge electrochemically to later be used as energy, powering our electronic devices. Electrode technology currently uses polymer binders to apply active material on the current collector. Polymers binders, commonly polyvinylidene fluoride (PVDF), are non-conductive carbon chains with resistances up to $3.6x10^{12}$ Ω, causing a loss of energy as charge flows through them. Furthermore the binder can be both chemically and mechanically degraded, resulting in a loss of contact between the active material and the current collector. This slowly lowers energy storage and the life time of the electrodes.

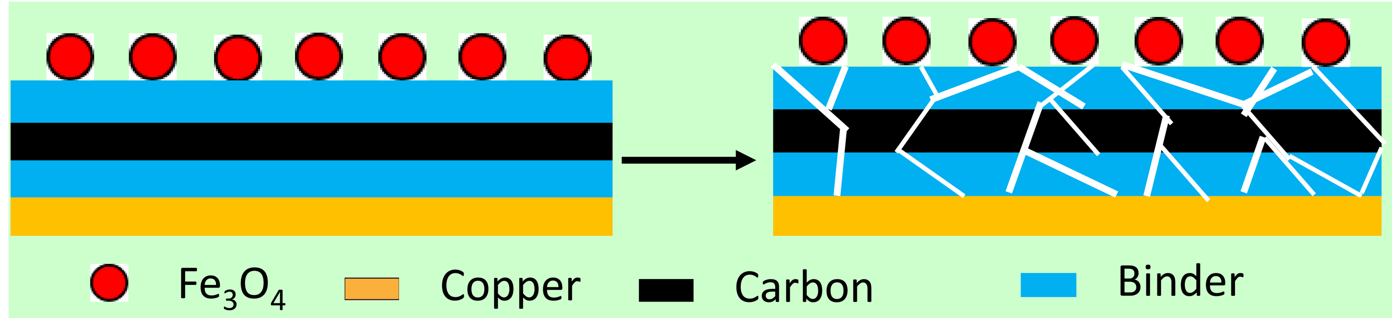

Figure 1: Electrode degradation after many cycles.

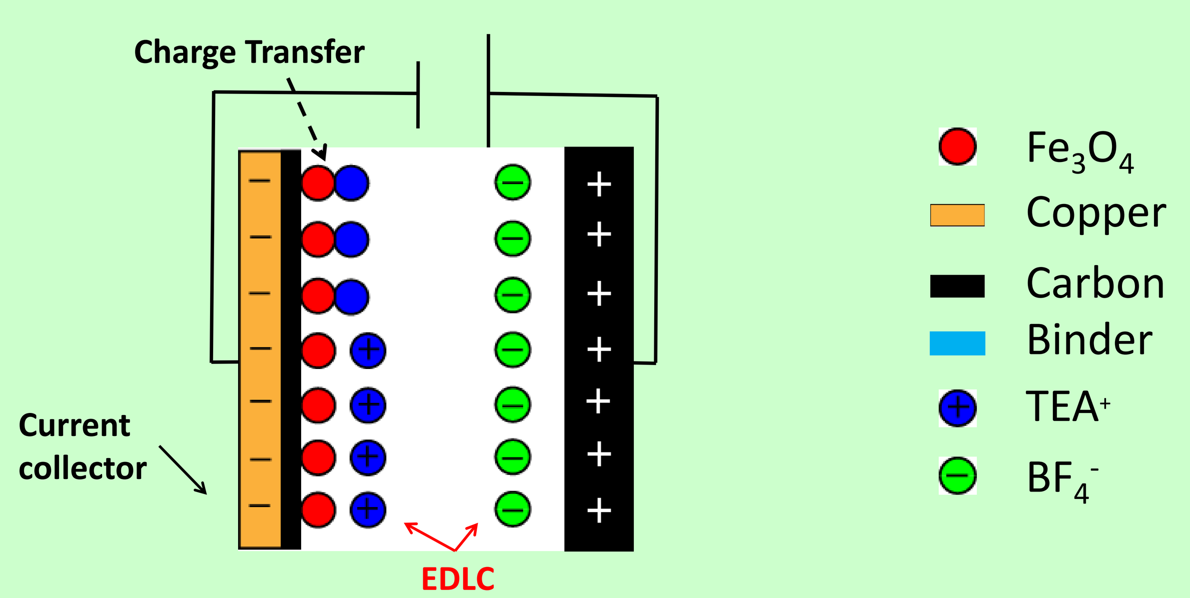

Figure 2: Schematic of a hybrid supercapacitor

This project proposes a synthesis of iron oxide nanoparticles hybridized directly onto graphene grown via chemical vapor deposition onto a copper substrate to be used as electrode of a supercapacitors. They were tested in a 2 electrode cell hybrid supercapacitor alongside electrodes made with purchased Fe_3O_4 nanoparticles and graphene, as well as graphene flake hybridized nanoparticles, the latter of the two using PVDF as a binder to apply the active material. We hope to show our electrodes are more stable compared to the use of a binder, while maintaining a greater percentage of the original capacitance over many cycles. This project seeks to continue the work by increasing the number of cycles to a life time of >1000 cycles and exploring different application methods of the active material.

Materials and Methods

Electrode Design

3 electrode cell & 2 electrode cell
Diamagnetic Current collectors: Copper and Graphite
Noncorrosive Organic electrolyte: Tetraethylammonium tetraboroflourate (TEA-BF4)

Graphene Flake Hybridized Nanoparticles Preparation

Graphene Flake synthesis
Nanoparticle synthesis via solvothermal process
Mass out active material: 90:10 ratio Fe_3O_4 :Binder
Sonication: 15 mins each, 3 times
Apply active material to copper via doctor blade method
Put under vacuum 1 hour, bake at 80°C overnight

Binder Free Graphene Hybridized Nanoparticles

Graphene Chemical Vapor Deposition (CVD) onto copper substrate
Nanoparticle Synthesis via solvothermal process.

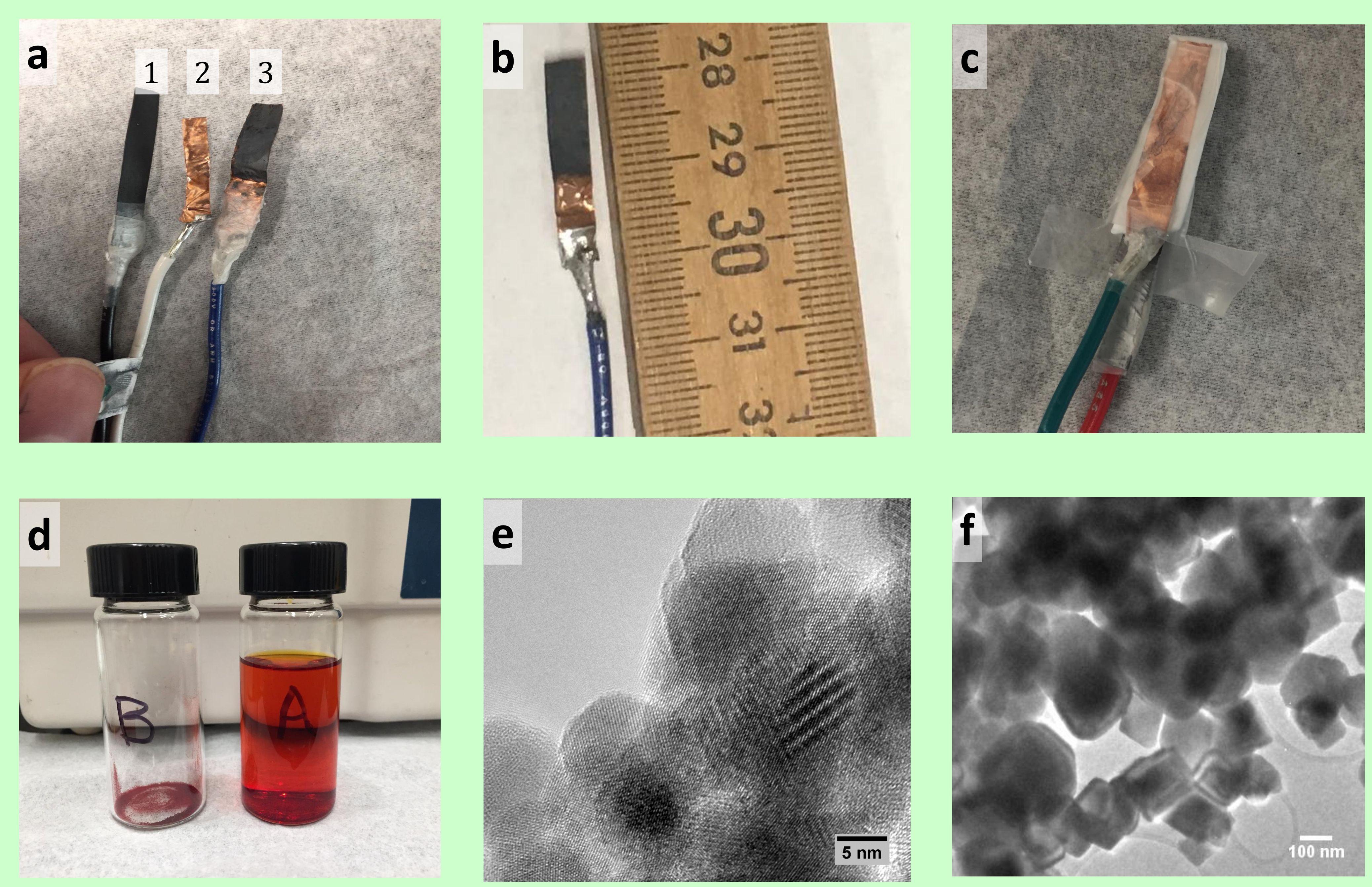

Figure 3:

(a) Carbon counter electrode (1) Binder free electrode (2) Graphene Flake/binder electrode (3), (b) Standard size of electrodes, (c) Example of 2 electrode cell configuration, (d) Precursor for solvothermal reaction, dry precursor (left) and precursor suspended in ethanol (right), (e) TEM images of solvothermal Fe_3O_4 nanoparticles with a size distribution of 10-15 nm and, (f) TEM of Commercially purchased Fe_3O_4 nanoparticles with a size distribution of 50-200 nm.

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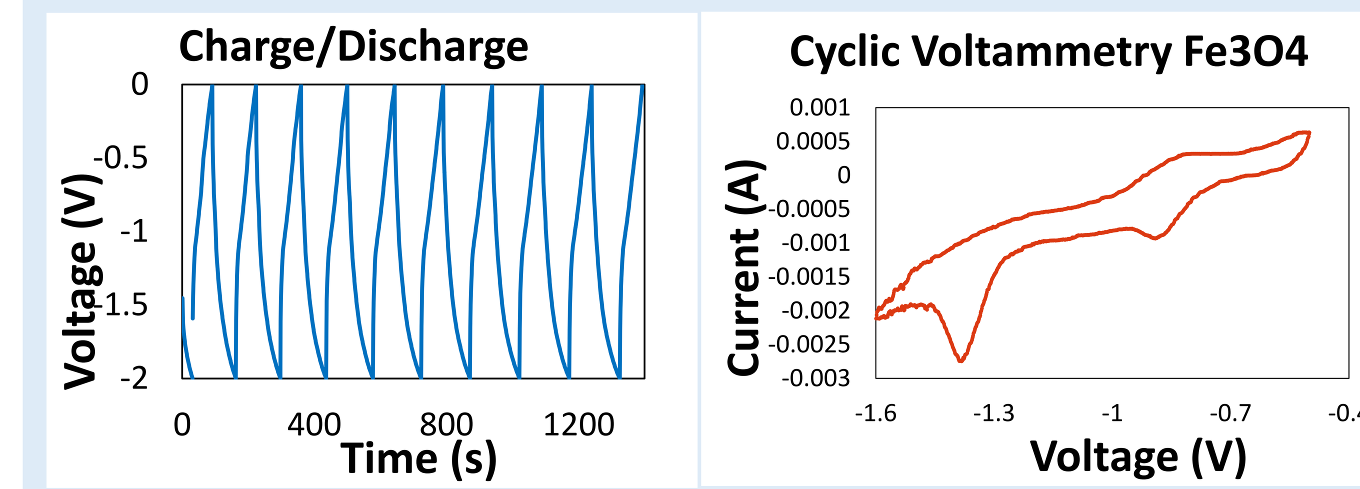
Results and Discussion



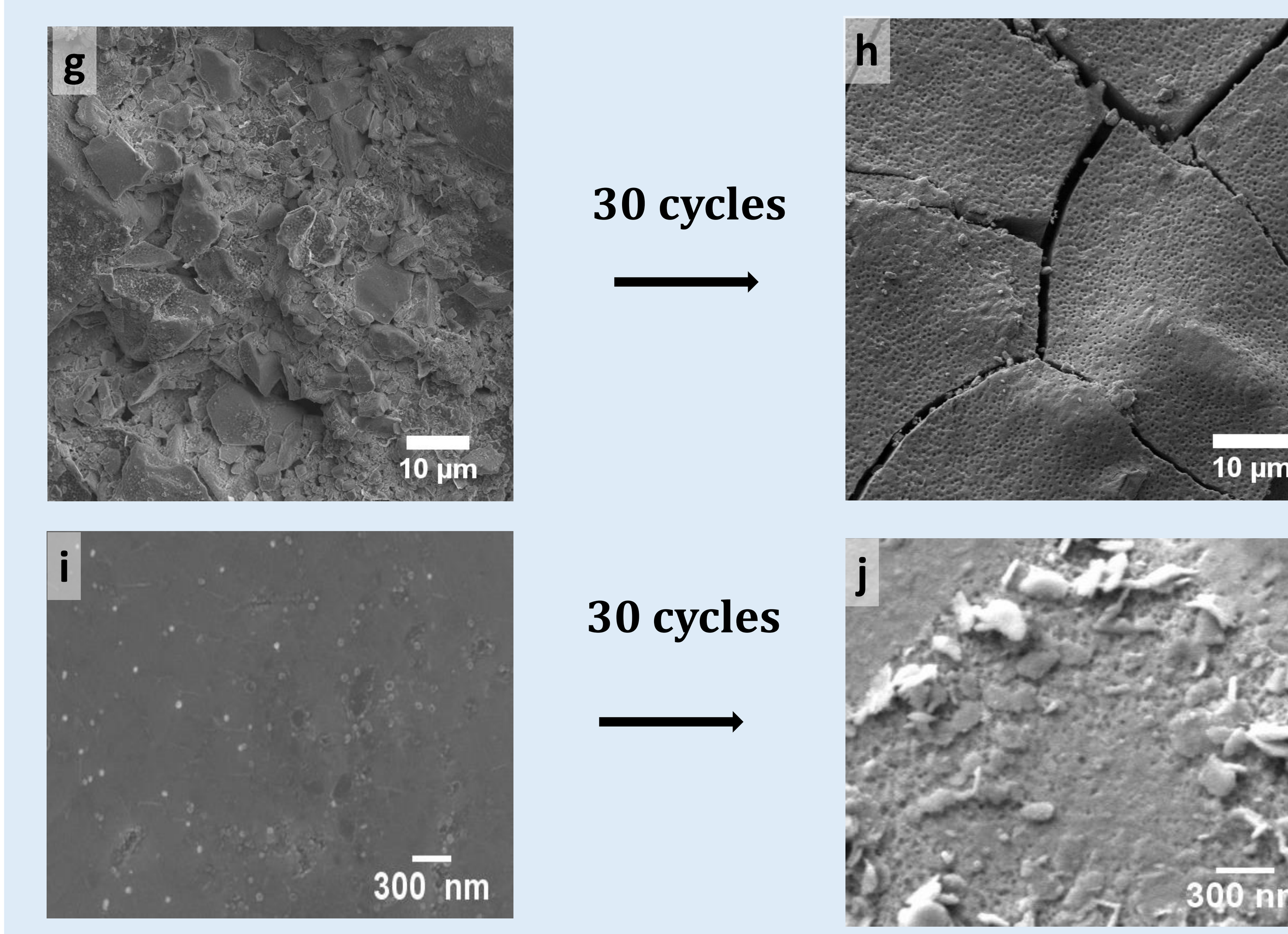
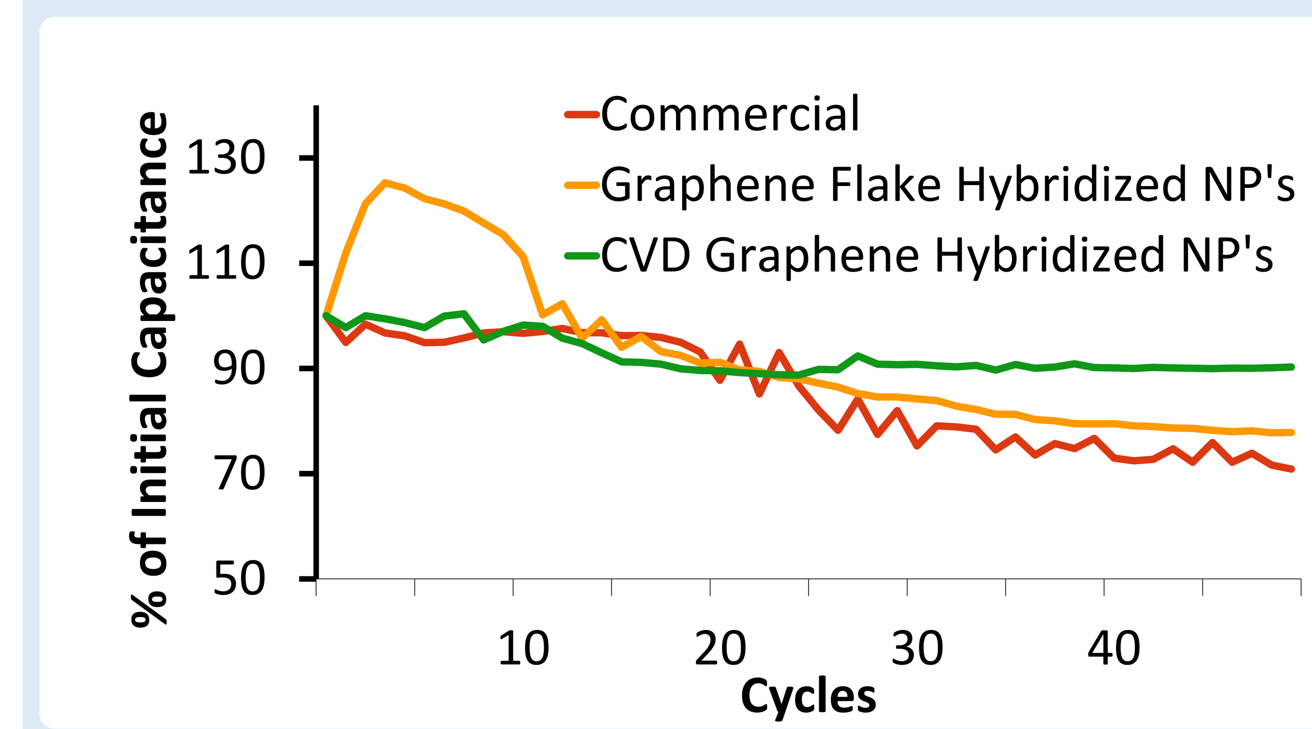


Figure 4:

(g) Graphene Flake/binder electrode pre-cycling (h) Graphene Flake/binder electrodes after 30 cycles (i) CVD Graphene electrode pre-cycling (j) CVD graphene electrode after 30 cycles



Conclusion

Preliminary testing show, after 50 cycles the binder free electrodes maintained 90.2% of the original capacitance where the graphene flake hybridized and commercial graphene and nanoparticles maintained 77.8% and 70.9% respectively. Future work will involve testing lifetime cycling >1000 cycles and exploring different application methods of active material.

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